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Bias-dependent photoluminescence in CdTe photovoltaics

Diana Shvydka,[a] V. G. Karpov, and A. D. Compaan
Department of Physics and Astronomy, University of Toledo, Toledo, Ohio 43606

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We show that external bias significantly affects the photoluminescence (PL) in CdTe photovoltaics. The main observations are: (1) reverse bias suppresses PL, (2) PL increases with moderate forward bias and tends to saturate when it is above the open-circuit voltage, and (3) PL in the region of saturation is extremely sensitive to device degradation. We attribute the observed phenomena to the competition between the field-induced separation of electrons and holes and their nonradiative recombination. We have developed a model that describes bias-dependent PL more quantitatively and forms a basis for using it as an indicator of device degradation. [DOI: 10.1063/1.1475359]

One distinctive but yet poorly described feature of photoluminescence (PL) in semiconductor devices is that both the carrier excitation and radiative recombination may occur in the region of high electric field. Most PL studies in semiconductors have been performed on single crystals or individual films in which high electric fields are absent.[1] One exception to this occurs with surface depletion layers.[2,3] Typically, the surface field is difficult to modify and even relatively high laser power densities do not effect much change when surface recombination velocities are high.[4,5] However, studies of InP (Ref. 3) and photochemically treated GaAs surfaces[6] have clearly shown increases in PL signal as the surface is unpinned and the surface field is decreased. In completed devices at the open circuit where interface recombination is not too great, typical focused laser powers are sufficient to short out the built-in fields of completed devices. This was the case, e.g., in our earlier studies of junction PL.[7]

In this letter, we present a study of junction PL from a CdTe/CdS junction where the energy gaps of CdTe and CdS are 1.5 eV and 2.4 eV at room temperature. In this case, a laser light of wavelength 752 nm (1.648 eV) is transparent to the CdS and is absorbed in the CdTe with an absorption length of $\alpha^{-1} \sim 0.3\,\mu$m. This is much narrower than the depletion layer width $\sim$1–3 μm in the lightly *p*-doped CdTe. The existence of a transparent conducting contact (SnO_2:F) to the CdS and the back contact (typically Cu/Au) to the CdTe allows us to control the electric field at the junction by the application of external bias.

The nonequilibrium electrons and holes are spatially separated by the junction electric field. PL is determined by their distribution overlap when the nonradiative recombination is relatively inefficient. In the opposite limiting case, the PL intensity is driven by the nonradiative recombination before the electrons and holes are spatially separated. By varying the external bias and thus changing the field, one can expect to observe the crossover between the two regimes. In this letter, we present data which indeed show the aforementioned crossover. The crossover is found to be very sensitive to the material degradation. We also develop a semiquantitative theory of the phenomenon.

The polycrystalline thin-film devices were prepared by two different techniques: vapor transport deposition and radio frequency magnetron sputtering. In both cases, a layer of CdS followed by a CdTe layer was deposited on commercially available SnO_2-coated glass substrates. The transparent conductive oxide layer served as a front electrode. After deposition, the samples were submitted to a standard anneal in the presence of $CdCl_2$ vapor which generally leads to improved electrical characteristics. Finally, a metal layer was deposited to form the back contact to CdTe. PL was excited with the 752 nm line of a Kr laser focused on the sample with a spot diameter of about 0.5 mm. The luminescence spectrum was collected at room temperature using a triple monochromator and charge coupled device detector. Applied external bias did not cause any significant change in the spectrum of the PL; therefore, we used the integral PL intensity in our data analysis.

The measured bias-dependent PL intensity $I(V)$ shows three distinct features (Fig. 1): (i) rapid increase at $V < V_{oc}$, the open-circuit voltage V_{oc} being in the range of 700 to 800

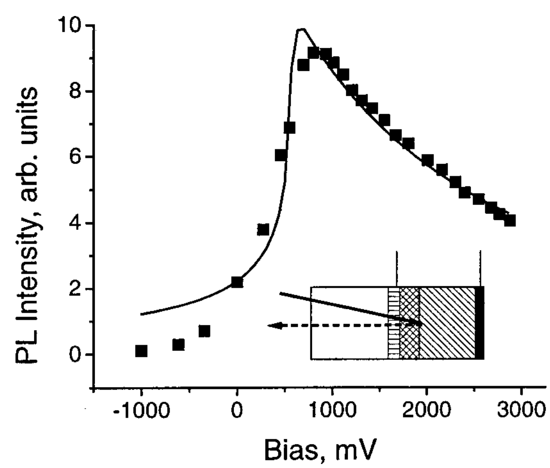

FIG. 1. Measured PL intensity in a wide range of applied biases for an unstressed device. Solid line represents analytical fit by Eq. (2). Inset shows PL measurement geometry with layers from the left- to right-hand side; glass, SnO_2:F, CdS, CdTe, and metal contact. Bias voltage is applied between SnO_2:F and metal.

[a]Electronic mail: dshvydka@physics.utoledo.edu

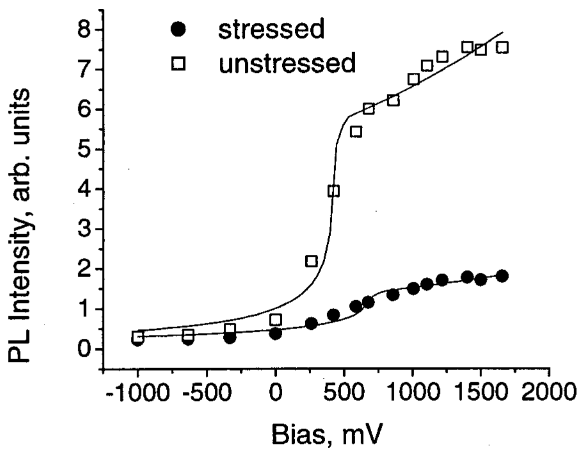

FIG. 2. Measured PL intensities vs bias before and after 28-day light-soak stress. Solid lines represent analytical fits by Eq. (2).

mV, (ii) the subsequent saturation, and (iii) gradual decrease in the far forward bias region. The latter trends are similar to the observations in InP Schottky diodes.[3] While retaining these qualitative features, the particular $I(V)$ shapes varied considerably between different samples without a significant difference between the vapor transport deposited and sputtered ones. This is illustrated by comparing the data in Figs. 1 and 2, the latter showing a more extended saturation region. A remarkable feature in Fig. 2 is that PL in the saturation region is extremely sensitive to light-soak-induced degradation: a change by almost one order of magnitude is observed in response to a 1-month light soak, which typically causes several percent change in the device efficiency, in accordance with the published data.[8]

The nonequilibrium carrier concentration responsible for the bias-dependent PL is described by the balance equation (see, for example, Ref. 9) that includes electron–hole generation (g), drift, and recombination and is equally applicable to electrons and holes,

$$g(x) - \mu E \frac{\partial n}{\partial x} - \frac{n}{\tau} = 0,$$

$$g(x) = g_0 \Theta(x) \exp(-\alpha x). \tag{1}$$

Here, μ and E are the mobility and the electric field, n is the concentration, τ is the nonradiative recombination time, $\Theta(x)$ is the step function, and the origin is at the metallurgical junction ($x>0$ corresponds to CdTe). In Eq. (1), we have adopted approximations which allow for analytical solutions while retaining the essential physics: (i) linear recombination kinetics, (ii) uniform electric field, and (iii) negligible role of diffusion. The boundary conditions are that the electron and hole concentrations remain finite everywhere. Solving Eq. (1) gives

$$I(V) \propto \int n_e n_h dx = \frac{g_0^2 \tau_e \tau_h}{\alpha(\alpha \ell_e + 1)(\alpha \ell_h + 1)}. \tag{2}$$

Here $\ell_{e(h)} = \mu_{e(h)} |E| \tau_{e(h)}$ is the electron (hole) drift length. Equation (1) indeed predicts PL intensity dominated by either the recombination or drift for the cases of low $[E \ll 1/(\alpha\mu\tau)]$ and high $[E \gg 1/(\alpha\mu\tau)]$ electric field, respectively.

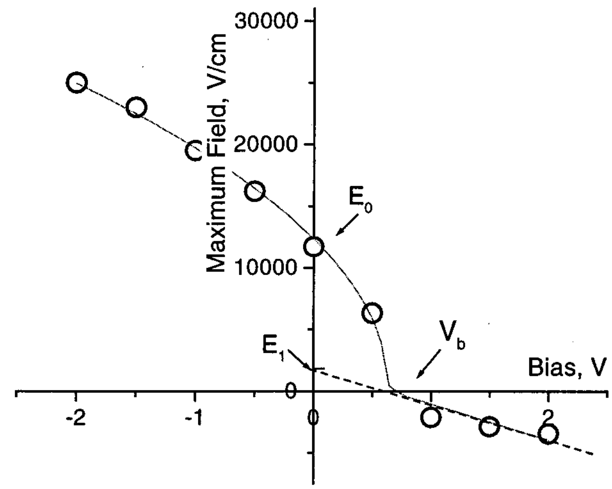

FIG. 3. AMPS-1D simulated data on the field-bias dependence for a CdTe/CdS solar cell (dots) in comparison with the piece-wise approximation in Eqs. (3) and (4) (solid line).

Note that for the case of heterojunctions (corresponding to our CdS/CdTe devices), the reverted field situation is more complex than predicted by Eq. (2), since a kink in the energy band structure near the metallurgical junction forms a barrier that makes it difficult for either one or both types of charge carriers to move into the opposite type region.[9] Fluctuations in the barrier penetrability may cause the observed variations in the $I(V)$ shapes between different samples (examples being the shapes in Figs. 1 and 2). This situation will be analyzed more in detail elsewhere.

For the case of reverse or moderate forward bias, the depletion region represents the most resistive part of the device and the bias drops there almost entirely. Because the depletion region width is proportional to the square root of the voltage drop, the maximum electric field becomes

$$E(V) = E_0 \sqrt{1 - \frac{V}{V_b}} \quad \text{for } V < V_b. \tag{3}$$

The built-in potential V_b is typically close to V_{oc}. As the forward bias balances the built-in field, it distributes more uniformly across the device. This leads to the field-bias dependence that is close to linear,

$$E(V) = E_1 \left(\frac{V}{V_b} - 1 \right) \quad \text{for } V > V_b. \tag{4}$$

E_0, E_1, and V_b are considered the device parameters. To verify the predictions in Eqs. (3) and (4), we performed numerical simulations by the AMPS-1D software[10] for realistic device parameters. The example in Fig. 3 is consistent with Eqs. (3) and (4).

To fit the data, we used the dependence in Eq. (2) with the piece-wise approximation for the electric field in Eqs. (3) and (4). The four fitting parameters $\ell_0 = E_0 \mu \tau \alpha, \ell_1 = E_1 \mu \tau \alpha$, V_b, and $I_0 = g_0^2 \tau_e \tau_h \alpha^{-1}$ were set the same for the electrons and holes. Adjusting them independently for each of the two could further improve the fit; however this could hardly be justified given the rather approximate character of our model. With that in mind, we find the fits in Figs. 1 and 2 quite satisfactory; the gradual decrease in $I(V)$ predicted by the model falls beyond the experimental region in Fig. 2.

Typical of our data were V_b slightly smaller than V_{oc}, $\ell_0 \sim 1$, and $\ell_1/\ell_0 \sim 0.1$, consistent with the available data on the CdTe parameters.[9] We also observed that the best-fit parameters, I_0, ℓ_0, and ℓ_1 decreased with degradation, such that I_0, scaled approximately as the square of ℓ_0. This observation is consistent with the prediction in Eq. (2) if we assume that the change in the recombination times is the main effect of degradation on the observed PL (the latter changed approximately by the factor of 3 under condition of this work).

In conclusion, the external bias is shown to significantly affect PL in CdTe photovoltaics. Our data are consistent with the model where PL is suppressed by two competing mechanisms: field-induced spatial separation of charge carriers and their nonradiative recombination. We have observed the crossover between the two mechanisms. We have also developed a semiquantitative model of bias-dependent PL. The main effect of degradation is found to be a decrease in the nonradiative recombination lifetime (possibly by introducing new recombination centers). We emphasize that the defects become visible when the junction field is suppressed by the external bias, which finding can have more general significance. In particular, the analogous situation seems also to be approachable by studying the electroluminescence. Other ways of achieving the similar conditions would be measuring degradation when the charge generation is high enough to screen the junction field: electron-beam induced current is one such example.[11]

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[10] AMPS-1D is a software package developed by Penn State University and aimed at simulating semiconductor multilayer devices. It is now commonly used and is available at http://www.psu.edu/dept/AMPS.
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